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NASA Technical Memorandum 107696

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(NASA-TM-107696) OXIDATIVE N93-13441
STABILITY OF LARC (TM)-TPI FILMS
(NASA) 20 p

Unclas

G3/27 0130532

October 1992

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23665-5225

OXIDATIVE STABILITY OF LARC™-TPI FILMS

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Abstract

The oxidative aging of 50-µm-thick films of LARC-TPI was studied using conventional thermogravimetric techniques and measurements of plane-stress fracture toughness. It was shown that at high temperature, most of the toughness loss occured very early relative to the weght loss. The difficulties of interpreting TGA results in this regime and the problems of extrapolations to long times are discussed.

Introduction

LARC™-TPI, the condensation polymer of benzophenone tetracarboxylic dianhydride and 3,3'-diaminobenzophenone, is a thermoplastic polyimide with a unique combination of processability (1) and thermal stability (2). Consequently, it is being considered for composite applications that require elevated-temperature performance for up to 120,000 hours. Extrapolating properties to these times is a formidable problem.

Probably the simplest and most convenient technique for the study of thermal aging is Thermogravimetric Analysis (TGA). A number of methods have been developed to interpret and extrapolate TGA weight loss data. Exactly how and why weight loss is related to changes in mechanical properties is, unfortunately, not usually addressed.

This paper is a report on preliminary efforts to quantify the thermal stability of LARC™-TPI in neat resin form using both TGA and mechanical tests. The prospects for accelerated aging prediction will be discussed.

Experimental:

TPI amic acid in diglyme was obtained from Mitsui Toatsu Co. (inherent viscosity 1.0 dL/g at 0.5% in dimethyacetamide at 30°C). This stock solution was stored at 4°C. A lower-molecular-weight endcapped amic acid was made by stirring a portion of the stock solution overnight at room temperature with a small amount of phthalic anhydride. Inherent viscosity of the endcapped polyamic acid was 0.36 dL/g.

The extremely viscous amic acid solutions were diluted with DMAc, cast on glass plates, and imidized in an air-circulating oven for 1 hour each at 100, 200, and 300°C.

TGA was performed under flowing air (40 ml/min) on small pieces cut from the imidized films. The standard procedure entailed pre-heating and drying the sample at 100°C for 30 minutes before beginning the scan. Data from the Seiko TG/DTA 200 were transferred to a personal computer data base for replotting and analysis. For dynamic TGA, extent of conversion, α, was calculated as fractional weight loss relative to the sample weight at 300°C. In the isothermal experiment, weight loss was reported relative to the weight at the end of the drying period.

Aging of imidized films was carried out in air-circulating ovens. Film edges were clamped loosely to a steel plate to prevent tearing and curling. Plane-stress fracture toughness was determined using single-edge-notched specimens (3).

Results and Discussion:

Typical TGA weight-loss traces are shown in Fig. 1. Comparison of the curves for the endcapped and unendcapped polymers reveals no consistent differences. This is a significant finding, since it indicates that our major conclusions will be independent of molecular weight, and are thus characteristic of the inherent stability of the polymer backbone. Interestingly, the comparison also suggests that the course of the degradation reactions was not affected by a change in polymer chain end groups. It is possible, of course, that at still higher concentrations of end-groups an effect might be seen.

Several of the TGA experiments were replicated starting with films of different thicknesses and with different sample weights. Changes of well over a factor of two in the amount of exposed surface area in the TGA pan did not affect the results significantly. We can conclude, therefore, that neither diffusion of oxygen into the films nor escape of volatile products was rate-limiting in the present experiments.

Before proceeding to the quantitative treatment of the TGA data, it is useful to examine the shapes of the curves in Fig. 1. All of the TGA thermograms were qualitatively similar to these. The primary peak in each derivative curve is skewed toward higher temperatures; in fact, it appears that there may be a slight shoulder on the low-temperature side (near 580°C at this heating rate). A sample that had been heated briefly to 380°C also shows this shoulder, so it is not thought to be an artifact due to solvent or similar impurities. Although two reactions are not resolved, the appearance of this peak gives the first indication that the weight-loss process may not be a simple one. Of course, even when the degradation kinetics are well-behaved, weight-loss of polymers can be hard to interpret, since it involves volatilization of small fragments-- fragments that must result from multiple scission events (4,5).

Flynn and Wall, in their critical survey of TGA analysis methods (6), recommend a plot of the rate of weight loss against conversion (or fractional weight loss) as diagnostic of a number of features of the reaction. Such a plot is given in Fig. 2. The small shoulder at low conversions is again visible. The concavity of the plot at small α is characteristic of an apparent negative order (i.e. of a rate that initially rises with conversion.) Polymer degradation studies often show this behavior: the isothermal rate would go through a maximum as a function of conversion or time. For example, Bruck's isothermal weight-loss curves for Kapton show a maximum rate at 60% conversion (7).

Because all reactions approach zero order at small conversions, Fig. 2 can also be used to obtain a preliminary estimate of E, the activation energy for the reaction, without knowing the reaction order. The slope of this plot near the origin is proportional to $E / \overline{T}^2$. Where $\overline{T}$ is the average temperature over which the slope is determined. A related, but more accurate, procedure is to plot $-d\alpha/d(1/T) = T^2\,(d\alpha/dT)$ vs. α. The slope of this plot is $E/R + 2\overline{T}$,where R is the gas constant. A representative data set is shown in Fig. 3, in which the vertical axis has been rescaled for convenience. As always, there is some uncertainty involved in drawing a tangent to an experimental curve. In this case, the slope is continually increasing with α, so the wider the range of α included in the fit, the higher the fitted slope tends to be. The uncertainties given in Table I reflect the lack of repeatability in the tangent-drawing procedure.

An apparent activation energy can also be determined by using data obtained at several heating rates. One method is to plot the logarithm of the heating rate against the inverse of the temperature at which a specified degree of conversion was reached (6). The slope, m, of the line is related to the apparent activation energy E via $E = -4.35\ m$ cal/mol. Like other so-called integral methods, this technique has the disadvantage of being sensitive to the choice of starting point. In Figure 4, least-squares lines were calculated for each value of α and the results are summarized in Fig. 5. A close examination of the data suggests, however, that the plots may not quite be linear. There may be a change in slope at the lowest heating rate. This apparent change in mechanism with rate (and thus with temperature) is exactly why accelerated testing must be approached with caution. Even if we take the numbers in Figure 5 at face value, it is clear that a simple kinetic model cannot be used over the entire range of conversion.

The question then arises as to how to make use of the numbers in Table I and Fig. 5. For screening purposes, it has been customary to rate polymer lifetimes at a given extent of conversion -- often 10% weight loss. The arbitrariness of this procedure is obvious. What is worse, it may not be relevant to the end use at all. By the time a high-performance polymer has reached 10% weight loss, it will have been chemically altered almost beyond recognition. At only 2-3% weight loss in air, PMDA-ODA polyimide has undergone crosslinking-related reactions in 50% of the polymer repeat units (8). Mechanical properties, on the other hand, can be changed drastically by relatively small amounts of chain scission or crosslinking. For example, chemical changes in as little as 3% of repeat units and almost no weight loss produce an 80% toughness loss in polyethersulfone (9). It is prudent, therefore, to focus on the very early stages of oxidative aging, and to carefully relate the weight loss to expected losses in mechanical properties.

The following experiment illustrates how this might be done. TPI films were aged in air at 400°C for 0,1 and 2 hours. Under these conditions, the films rapidly darkened and embrittled, although a parallel isothermal TGA experiment indicated a weight loss of only 3% in three hours. The zero-time toughness agreed well with a previous determination (3); the time dependence is shown in Figure 6. A detailed kinetic law cannot be derived from such a limited data set, so for simplicity, the results have been fitted to a pseudo-first-order decay with a half life of 1.5 hours. This seems reasonable: at the same temperature, Kapton would exhibit a half-life of 2 hours (as measured by the fall-off in its ultimate elongation.) (10)

Comparing the TGA and mechanical measurements for TPI, we conclude that during the first 3% weight loss, its toughness would fall to one-fourth of its initial value.

With this result, we are now in a better position to make use of the data in Table I and Figure 5. From these data, it appears that an apparent activation energy of 20-25 kcal/mole would describe the weight-loss data in the earliest stages of the reaction. This is quite a bit lower than the 33-39 kcal determined by various methods for the degradation of Kapton (11). Many of these determinations apply to later stages of the reaction, however. For example, Bruck's determination was made at the maximum in the differential rate (i.e. at 60% conversion.) (7)

Assuming simple Arrhenius behavior with an activation energy of 30 kcal, the toughness half life extrapolates to 120,000 hours at 156°C. If the activation energy is as low as 20 kcal, the use temperature extrapolates to 110°C. Note that these are intended as "worst case" estimates, since they derive from thin films above T_g. In any real structure, oxygen transport will likely limit degradation rates. Polyimides are extremely stable in the absence of oxygen(12). Actually, there are some data bearing on this point. In a study of adhesive bonds (13), lap-shear strength was shown to be unchanged after 50,000 hours at 232°C. In practice, it is doubtful that a thermoplastic will be used above T_g-50°C. In this range, physical aging and long term behavior under load (creep) are of concern, but the present study suggests that chemical effects cannot be ruled out if oxygen is present.

This preliminary study leaves a number of unanswered questions. The first concerns the best way to characterize the early stages of the evidently complex oxidation reaction. Careful comparisons among chemically related materials may be of help here. Secondly, the kinetics of toughness loss needs to be confirmed. Future work will therefore attempt to verify the postulated Arrhenius behavior of residual mechanical properties. Finally, we must treat the complicated problem of oxygen diffusion in an evolving structure. For example, surface crosslinking may inhibit diffusion of oxygen and pyrolysis products; microcracking may increase the effective surface area over time.

References

1. Burks, H. D., St. Clair, T. L., and Hou, T. H., *SAMPE Quarterly* 18(1), 1 (1986)
2. St. Clair,T. L. and Progar, D. J., "Adhesive Evaluation of New Polyimides", *NASA Technical Memorandum 89140*, April 1987
3. Hinkley, J. A. and Mings, S. L., Polymer 31, 75 (1990)
4. Schneider, H. A., Ch. 10 in Degradation and Stabilization of Polymers, v.1, H.H.G. Jellinek, ed., Elsevier, Amsterdam, 1983 p. 506
5. Dine-Hart, R. A. and Wright, W. W., *Makromol. Ch.* 153, 237 (1972)
6. Flynn, J. H. and Wall, L. A., "General Treatment of the Thermogravimetry of Polymers", *J. Res. NBS-A* vol 70A, no. 6, 1966
7. Dine-Hart, R. A., Parker, D. B. V., and Wright, W. W., *Br. Polym. J.* 3, 235 (1971)
8. Bruck, S. D. *Polymer* 4, 435 (1964)
9. Hinkley, J. A. and Campbell, F. J., *J. Mater. Sci Lett.*2, 267, (1983)
10. Heathcock, J. F. and Berr, C. E., *SPE Trans.*, April, 1965, p.105
11. Traeger, R. K. and Salazar, E. A., *ACS Polymer Preprints* 12(2) 292 (1971)
12. Bruck, S. D., *Polymer* 5, 49 (1965)
13. Hendricks, C. L. and Hale, J. N., "High Temperature Adhesive Development and Evaluation", pp. 351-390 in Welding, Bonding and Fastening 1984, *NASA Conference Publication 2387*, John D. Buckley and Bland A. Stein, eds., 1985

Table I

Initial Activation Energies From Differential Weight-Loss Curves

rate, °C/min	range of α fitted	E, kcal/mol	
		as-received	endcapped
1.0	0.1	21.3±4.1	23.0±3.7
2.5	0.04	20.4±1.6	17.8
10	0.03	20.5±1.8	19.0±1.5
20	0.025	19.2±1.2	17.4±1.4
		20.4	19.3

Figure Captions

1a. Raw TGA data for as-received LaRC^{TM}-TPI. Heating rate 10°C/min

1b. Raw TGA data for endcapped LaRC^{TM}-TPI Heating rate 10°C/min

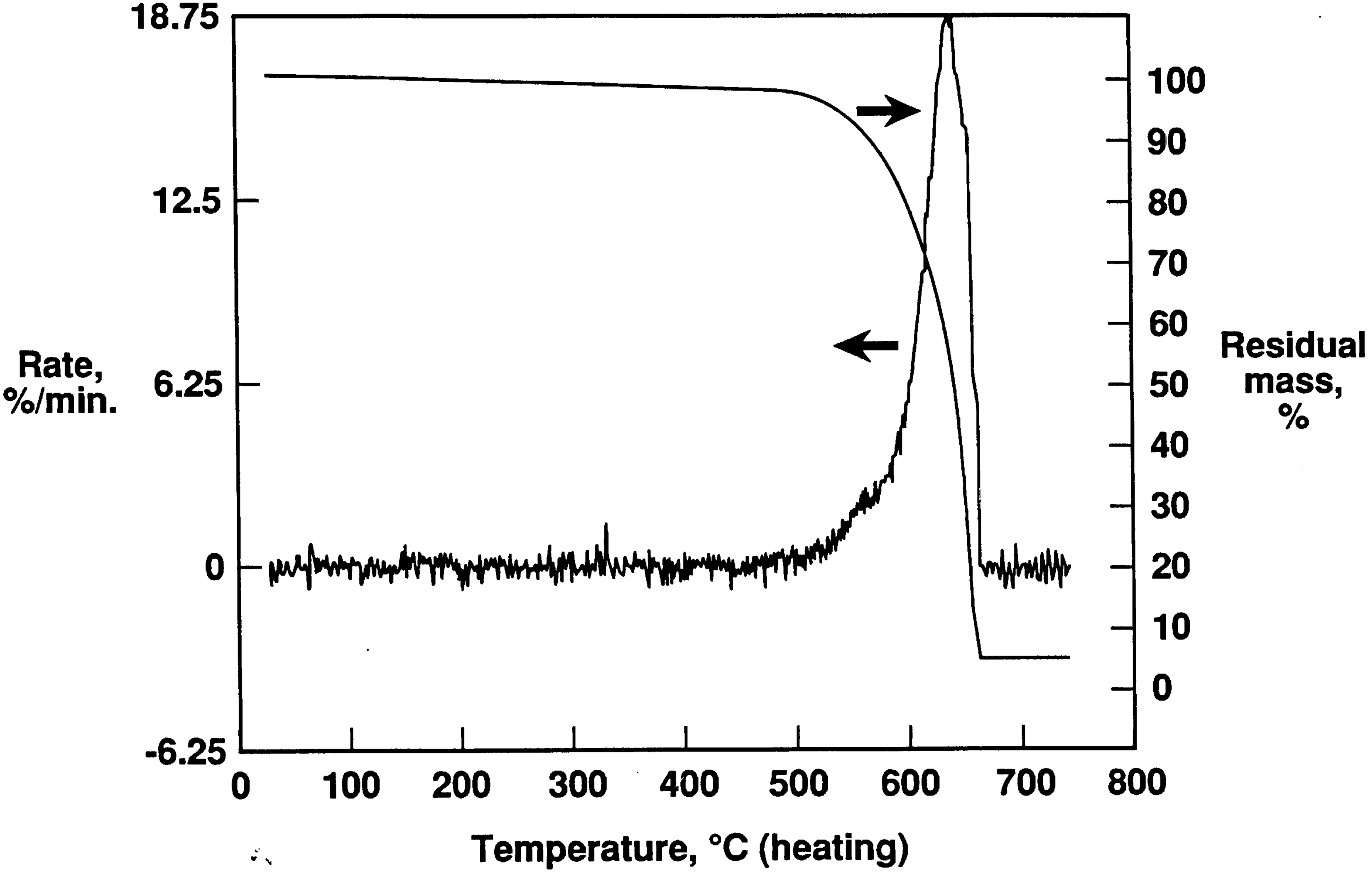
2. Differential weight loss as a function of conversion. Endcapped polymer, heating rate 10°C/min

3a. and b. Data of Figure 2 replotted as (T^2)(weight loss rate) vs conversion. Note that $dw/dt=(w_0)(-d\alpha/dT)(dT/dt)$, where w is the sample mass, w_0 is the mass at the start of the experiment, t is time, and dT/dt is the TGA temperature scan rate

4. Natural log of heating rate in °C/min vs inverse temperature at various conversions

5. Activation energies from slopes of heating rate plots like Figure 4

6. First-order plot of normalized room-temperature fracture toughness of 50µm films vs aging time at 400°C in circulating air



18.75
12.5
6.25
0
-6.25
Rate, %/min.
100
90
80
70
60
50
40
30
20
10
0
Residual mass, %
0
100
200
300
400
500
600
700
800
Temperature, °C (heating)

Figure 1a.

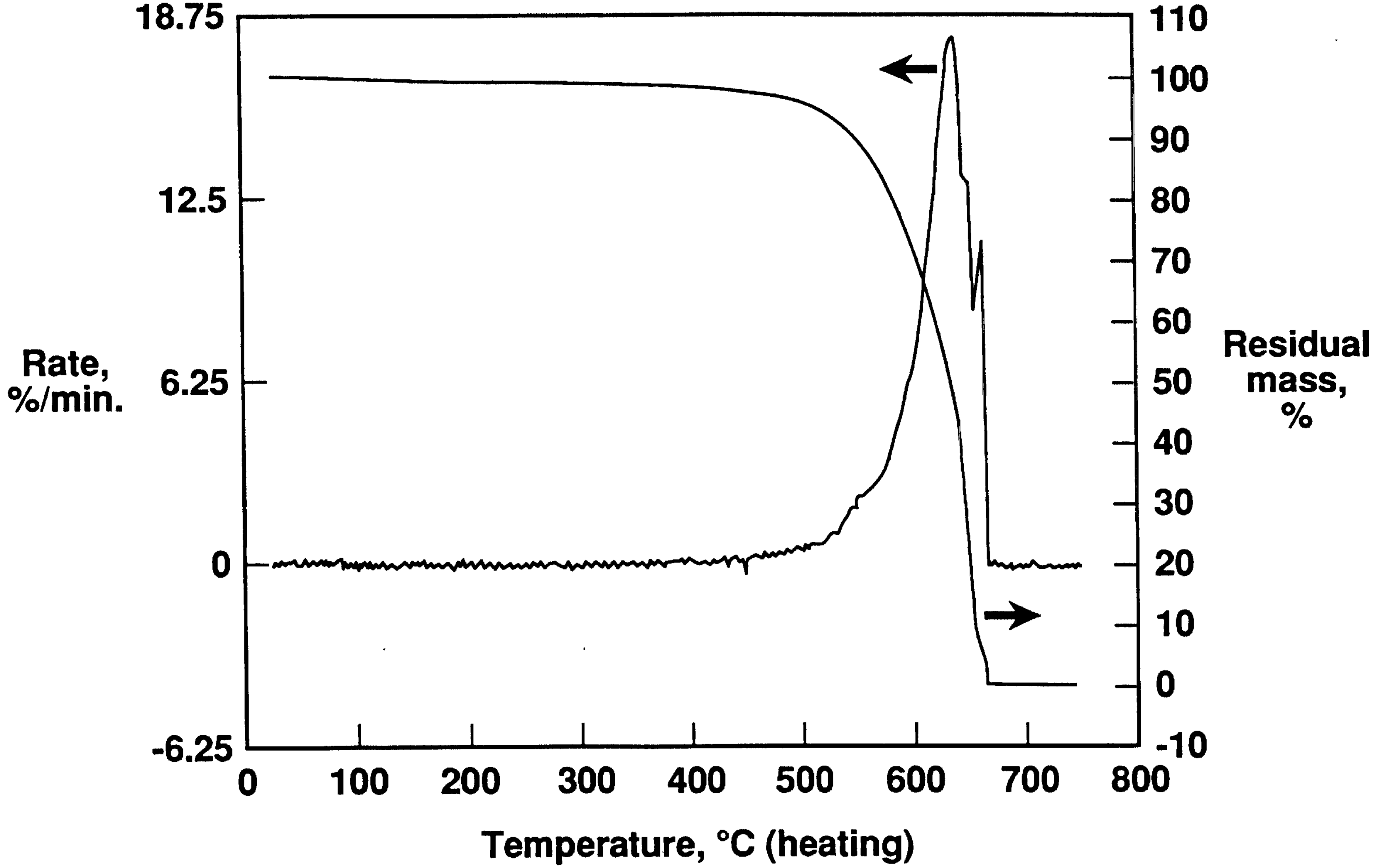


Figure 1b.

2/hinkley

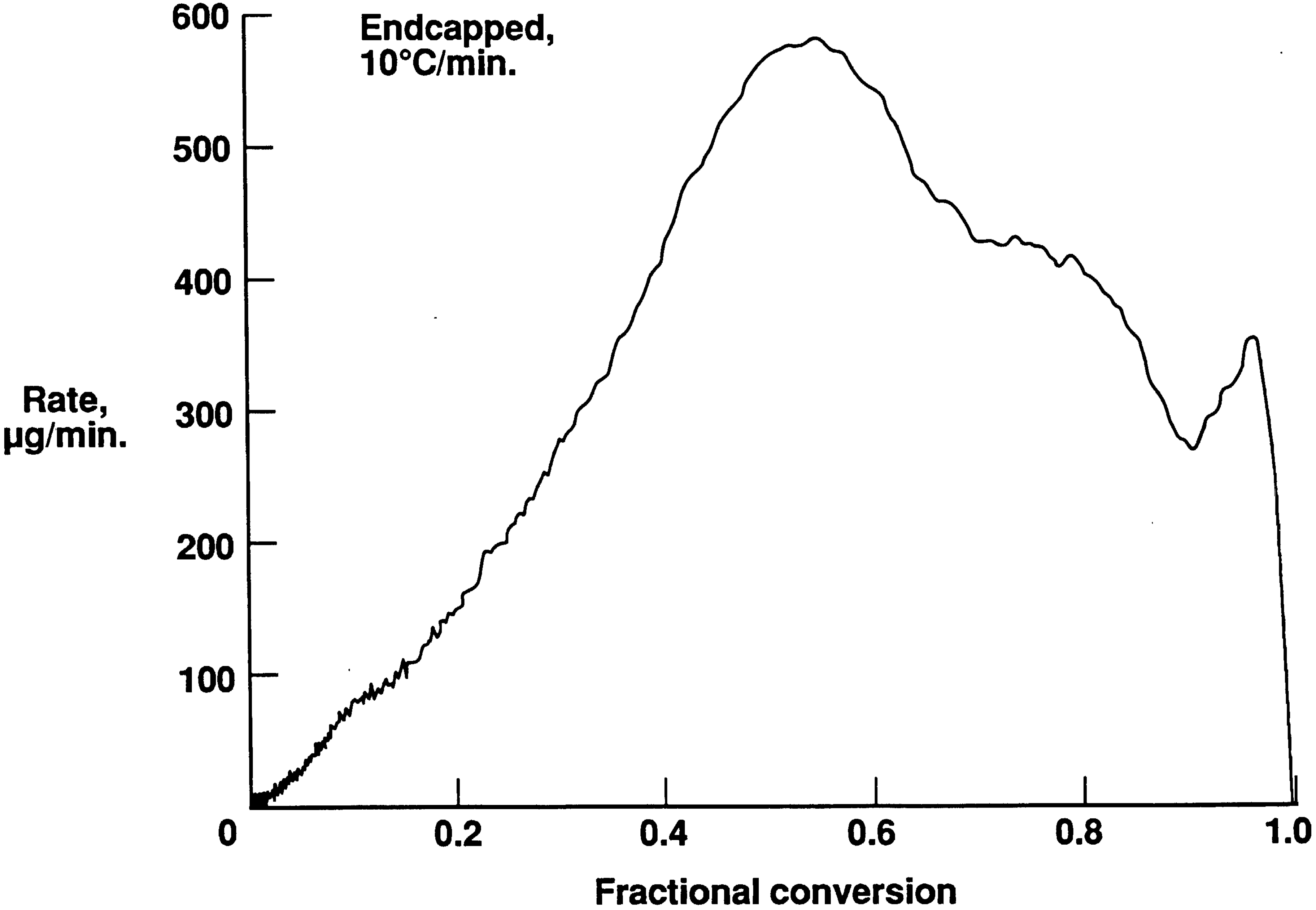

600
500
400
300
200
100
0
Rate,
µg/min.
Endcapped,
10°C/min.
0.2
0.4
0.6
0.8
1.0
Fractional conversion

Figure 2

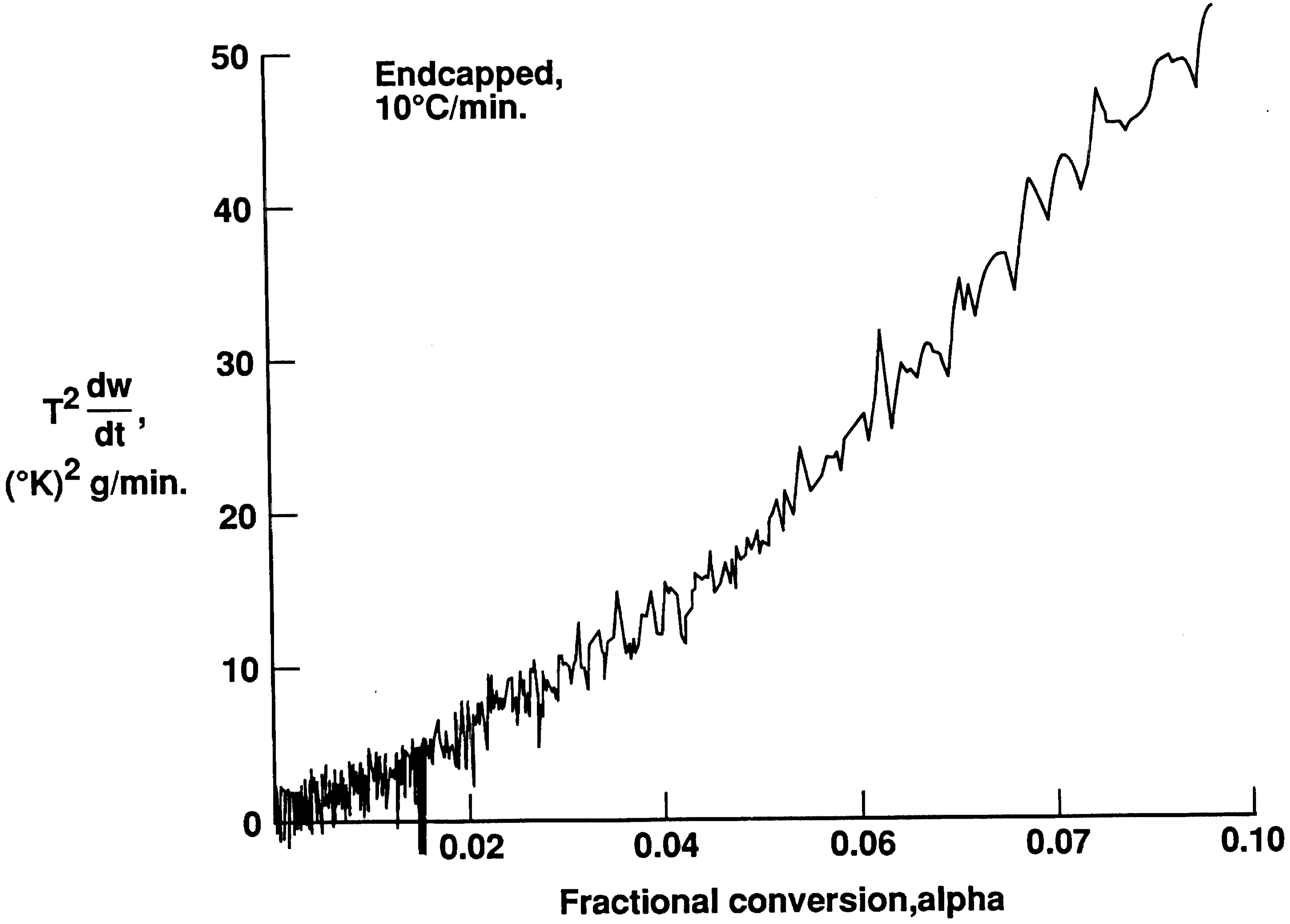


Figure 3a.

4/hinkley

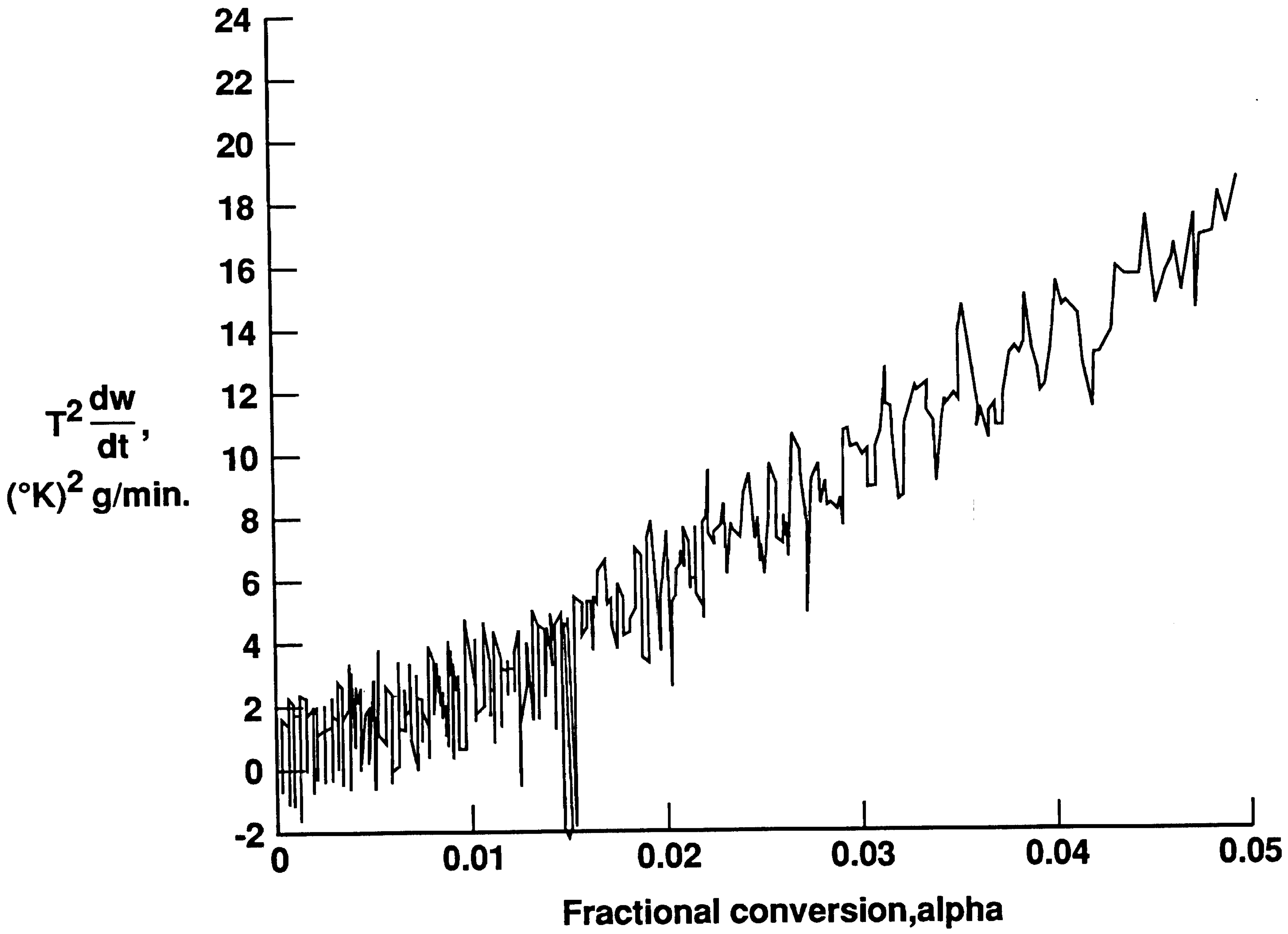

$T^2 \frac{dw}{dt}$,
(°K)^2 g/min.
24
22
20
18
16
14
12
10
8
6
4
2
0
-2
0
0.01
0.02
0.03
0.04
0.05
Fractional conversion,alpha

Figure 3b.

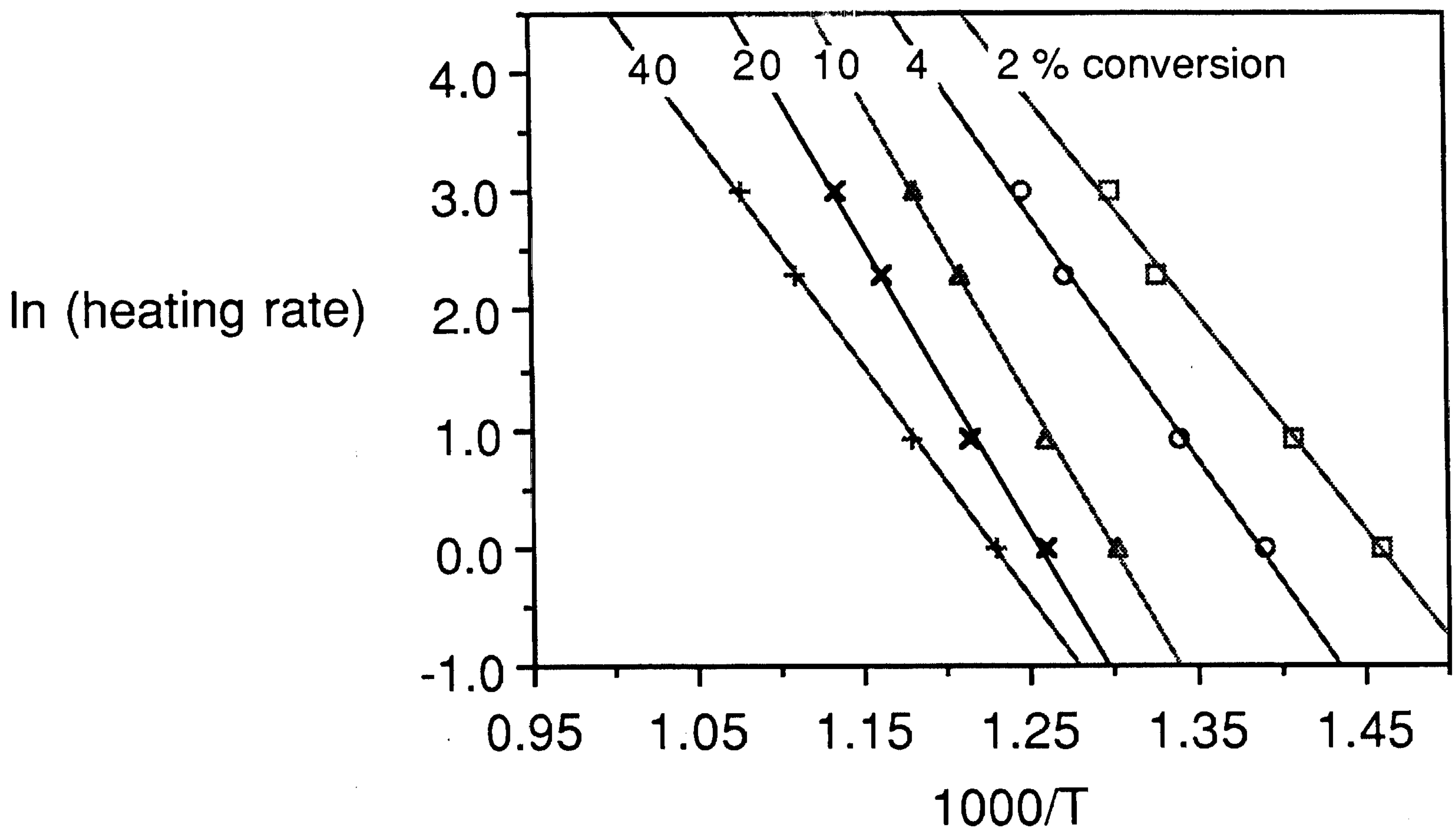

40
20
10
4
2 % conversion
ln (heating rate)
4.0
3.0
2.0
1.0
0.0
-1.0
0.95
1.05
1.15
1.25
1.35
1.45
1000/T

Figure 4.

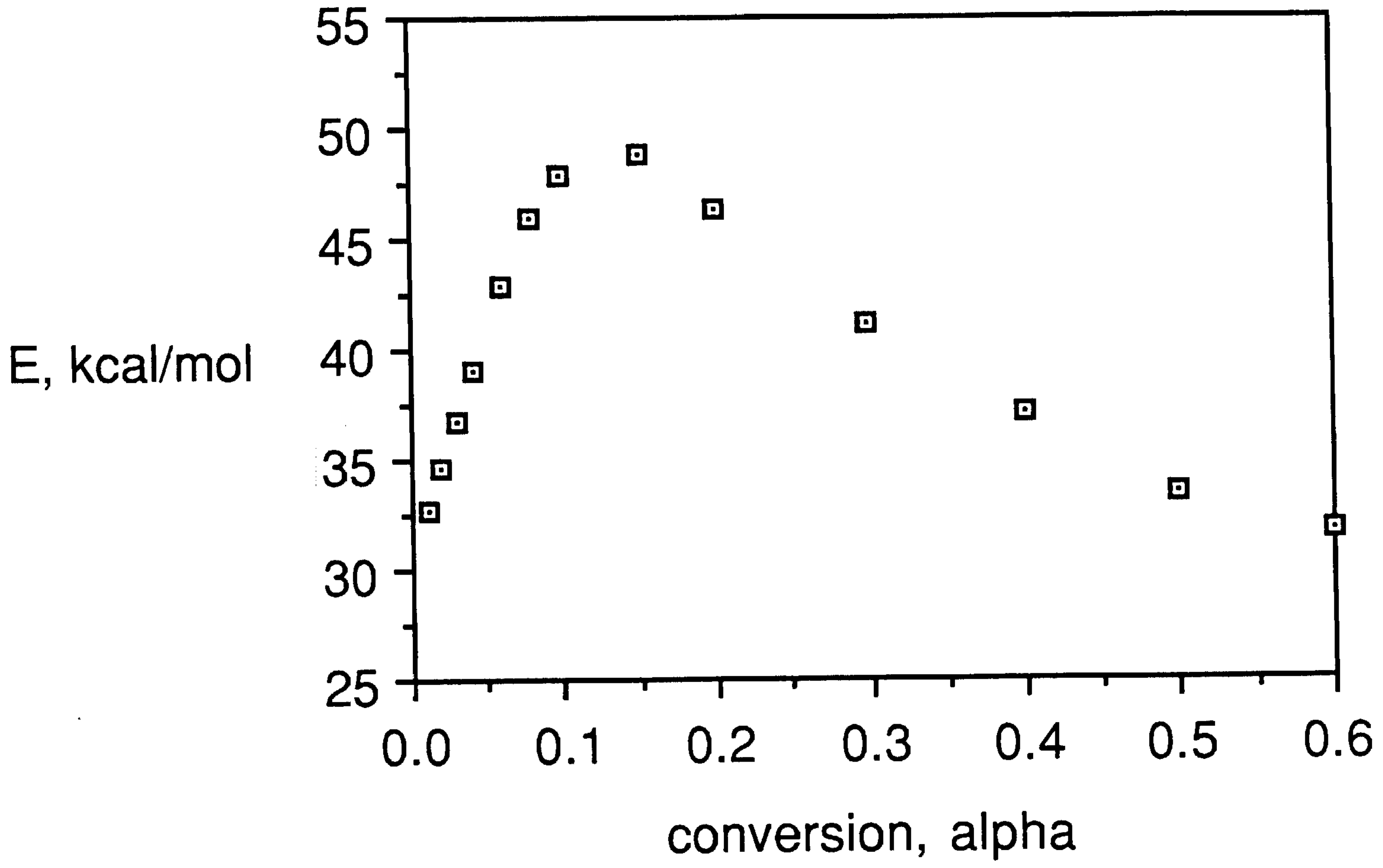

E, kcal/mol
55
50
45
40
35
30
25
0.0
0.1
0.2
0.3
0.4
0.5
0.6
conversion, alpha

Figure 5.

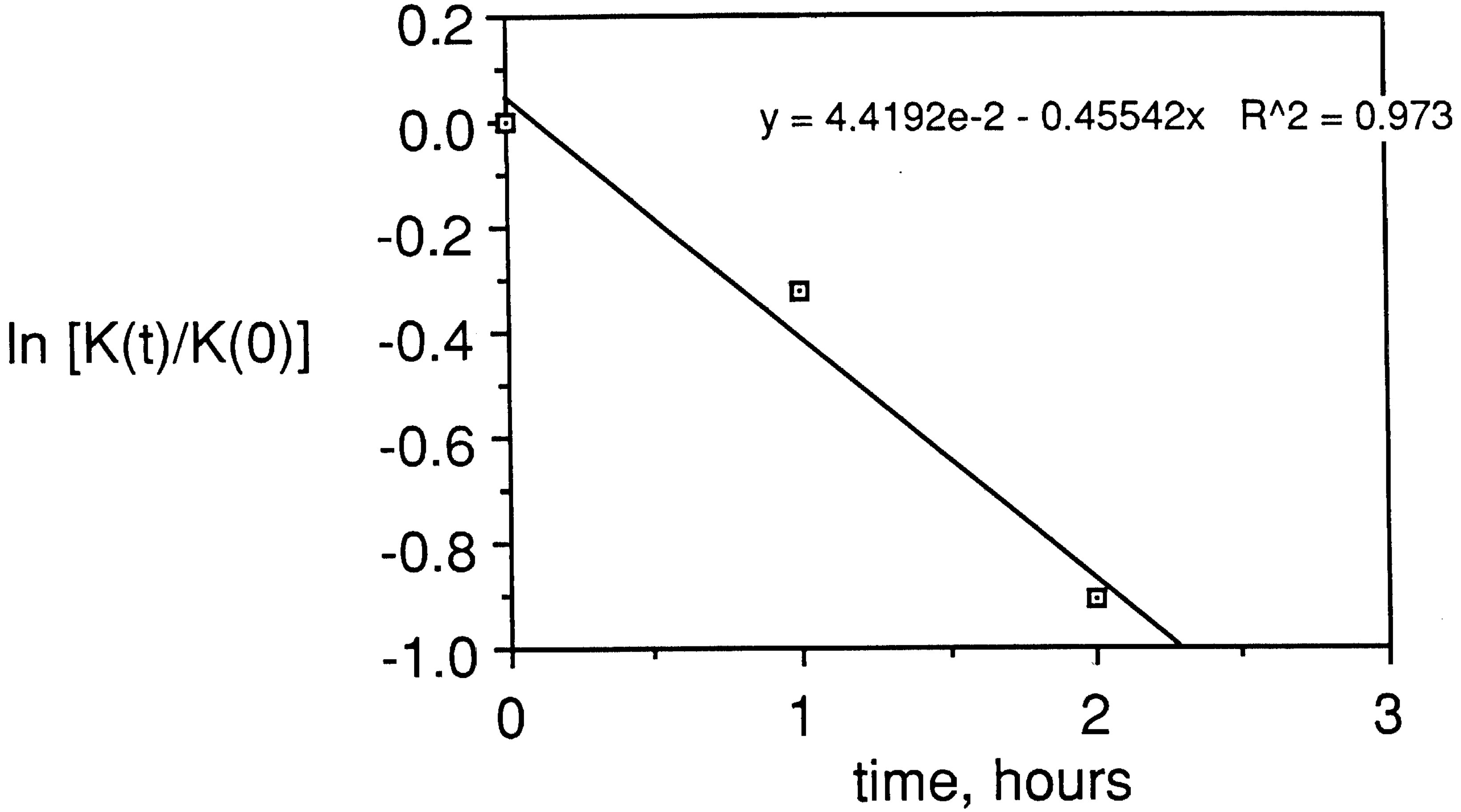

0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
ln [K(t)/K(0)]
0
1
2
3
time, hours
y = 4.4192e-2 - 0.45542x   R^2 = 0.973

Figure 6.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE October 1992	3. REPORT TYPE AND DATES COVERED Technical Memorandum

4. TITLE AND SUBTITLE
Oxidative Stability of LARC™-TPI Films

5. FUNDING NUMBERS
WU 506-43-11

6. AUTHOR(S)
J. A. Hinkley

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
NASA Langley Research Center
Hampton, VA 23681-0001

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Aeronautics and Space Administration
Washington, DC 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NASA TM-107696

11. SUPPLEMENTARY NOTES
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12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unclassified-Unlimited
Subject Category 27

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

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14. SUBJECT TERMS
thermogravimetric analysis, polyimide, oxidation, fracture toughness

15. NUMBER OF PAGES
19

16. PRICE CODE
A03

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT